

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 537 387 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
11.12.1996 Bulletin 1996/50

(51) Int Cl.⁶: **C10M 133/52, C10M 159/12**
// **C10N60/00, C10N60/12,**
C10N60/14

(21) Application number: **91309189.8**

(22) Date of filing: **08.10.1991**

(54) Modified dispersant compositions

Modifizierte Dispergierzusammensetzungen

Compositions de dispersant modifié

(84) Designated Contracting States:
BE DE ES FR GB IT

• **Rees, Mark**
Reading, Berkshire, RG5 4XW (GB)

(43) Date of publication of application:
21.04.1993 Bulletin 1993/16

(74) Representative: **Woods, Geoffrey Corlett et al**
J.A. KEMP & CO.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(73) Proprietor: **ETHYL PETROLEUM ADDITIVES**
LIMITED
Bracknell, Berkshire RG12 2UW (GB)

(72) Inventors:
• **Ryan, Helen Theresa**
Bracknell, Berkshire, RG12 2EJ (GB)
• **Scattergood, Roger**
Reading, Berkshire, RG7 1DP (GB)

(56) References cited:
EP-A- 0 271 937 **EP-A- 0 359 522**
EP-A- 0 438 847 **EP-A- 0 454 380**
US-A- 3 511 780 **US-A- 4 234 435**
US-A- 4 428 649 **US-A- 4 657 214**

EP 0 537 387 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

This invention relates to novel modified ashless dispersants, to processes for their production, and to their use in liquid hydrocarbonaceous media. As used herein, the term "ashless" is used in the normal art-recognized sense of denoting that the composition is devoid of metals such as alkali or alkaline earth metals, zinc or other metals that tend to produce metal-containing residues. In this connection, boron and phosphorus are not deemed to be metals as the compositions of this invention do contain boron and phosphorus.

A continuing problem in the art of lubrication is to provide lubricant compositions which satisfy the demands imposed upon them by the original equipment manufacturers. One such requirement is that the lubricant not contribute to premature deterioration of seals, clutch face plates or other parts made from fluoroelastomers. Unfortunately, and as is well known, basic nitrogen-containing dispersants such as succinimide dispersants commonly used in oils tend to exhibit a strong adverse effect upon fluoroelastomers, by causing them to lose their flexibility and tensile strength, to become embrittled, and in severe cases, to disintegrate. Contemporary test methods for evaluating fluoroelastomer compatibility of lubricants and functional fluids are the Volkswagen P.VW 3334 Elastomer Compatibility Test, the CCMC Oil-Elastomer Seal Test (CEC L-39-T-87), and the fluoroelastomer seal test in accordance with the TO-3 Caterpillar Specification.

Methods of post-treating various nitrogen-containing dispersants with various substances are well documented in the literature.

In accordance with this invention, there is provided an oil soluble dispersant composition formed by reacting concurrently or sequentially in any order a basic nitrogen-containing ashless dispersant (i) with at least one dibasic acylating agent containing up to 12, preferably up to 8, more preferably up to 6, and most preferably 4, carbon atoms, (ii) with at least one phosphorylating compound selected from phosphorous acid, hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid, hypophosphorous acid, pyrophosphorous acid, phosphinous acid, triphosphoric acid, tetraphosphoric acid, trimetaphosphoric acid, POCl_3 , PCl_3 and PBr_3 and (iii) with at least one boronating compound, such that the initial ashless dispersant is chemically modified via acylation in (i), by phosphorylation in (ii), and by boronation (often referred to as "boration") in (iii). In this connection, any two or all three of the reactions (i), (ii) and (iii) can be conducted concurrently, and when two of them are conducted concurrently, the third reaction can be conducted either before or after such concurrent reaction. The phosphorus compound or compounds react with the basic nitrogen-containing ashless dispersant to introduce phosphorus moieties into the dispersant. It is preferred to conduct the phosphorylation in (ii) using phosphorous acid, H_3PO_3 . Any suitable boron compound or compounds can be used provided it is or they are capable of reacting with the basic nitrogen-containing ashless dispersant to introduce boron moieties into the dispersant. Desirable materials for this use include one or more boron oxides, boron halides, boron acids, ammonium salts of boron acid, boron esters, and the like. The preferred material is boric acid (also known as orthoboric acid).

The preferred acylating agents used in the reaction identified as (i) above are maleic anhydride, maleic acid, fumaric acid, malic acid or any combination of any two, any three or all four of these compounds.

Ashless dispersants utilized in the foregoing processing include hydrocarbyl succinimides, hydrocarbyl succinamides, mixed ester/amides of hydrocarbyl-substituted succinic acids, Mannich condensation products of hydrocarbyl-substituted phenols, formaldehyde and polyamines, and amine dispersants formed by reacting high molecular weight aliphatic or alicyclic halides with amines, such as polyalkylene polyamines. Mixtures of such dispersants can also be used.

Such basic nitrogen-containing ashless dispersants are well known lubricating oil additives, and methods for their preparation are extensively described in patent literature.

The preferred ashless dispersants are hydrocarbyl succinimides in which the hydrocarbyl substituent is a hydrogenated or unhydrogenated polyolefin group and preferably a polyisobutene group having a number average molecular weight (as measured by gel permeation chromatography) of from 250 to 10,000, and more preferably from 500 to 5,000, and most preferably from 750 to 2,500. The ashless dispersant is most preferably an alkenyl succinimide.

Another embodiment of this invention is the provision of a dispersant prepared as above having the ability when formulated in a finished engine lubricating oil of satisfying the requirements of the ASTM sequence VE engine tests for API "SG" performance (see ASTM 315 H, part III Seq. VE), and the requirements of the Volkswagen P.VW 3334 Elastomer Compatibility Test and/or the requirements of the CCMC Oil-Elastomer Compatibility Test (CEC L-39-T-87) and/or the fluoroelastomer seal test in accordance with the TO-3 Caterpillar Specification.

Other embodiments of this invention involve the provision of lubricating oil additive concentrates containing an effective amount of an improved dispersant composition of this invention and an oil of lubricating viscosity containing an effective amount of the improved dispersant composition.

Still further embodiments of this invention are processes for producing the improved dispersant compositions of this invention. One such embodiment comprises reacting a basic nitrogen-containing ashless dispersant with (i) at least one dibasic acylating agent containing up to 12, preferably up to 8, more preferably up to 6, and most preferably

4, carbon atoms, with (ii) at least one phosphorus compound preferably at least one inorganic phosphorus acid or anhydride thereof, most preferably phosphorous acid, H_3PO_3 , and with (iii) at least one boron compound preferably at least one boron oxide, boron halide, boron acid, ammonium salt of boron acid, or boron ester, most preferably boric acid, said reactions being conducted concurrently or sequentially in any order such that the initial ashless dispersant is chemically modified via acylation, by phosphorylation and by boronation.

These and other embodiments and features of this invention will be apparent from the ensuing description and appended claims.

Basic Nitrogen-Containing Ashless Dispersants

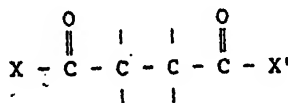
As noted above, the process of this invention can be applied to any basic nitrogen-containing ashless dispersant susceptible to acylation, phosphorylation and boronation. Thus the process can be applied to any of the basic nitrogen-containing dispersants referred to hereinabove.

The preferred basic nitrogen-containing dispersants utilized in the practice of this invention are the hydrocarbyl succinimides. As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between a hydrocarbyl substituted succinic acylating agent and a polyamine and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

Of the succinimides, those having an average of at least 3 nitrogen atoms per molecule are preferred. More preferred are those formed by use as one of the reactants of at least one aliphatic hydrocarbyl substituted succinic acylating agent in which the hydrocarbyl substituent contains an average of at least 40 carbon atoms. Preferably, the dispersant is a succinimide dispersant formed from an alkyl or alkenyl succinic acylating agent having an average of at least 40 carbon atoms in the alkyl or alkenyl group and an alkylene polyamine mixture having an average of at least 3 nitrogen atoms per molecule, more preferably a succinimide dispersant formed from a polyisobutenyl succinic acylating agent derived from polyisobutene having a number average molecular weight in the range of 500 to 10,000 and an ethylene polyamine mixture including cyclic and acyclic structures, said mixture having an average overall composition approximating to a mixture in the range of from triethylene tetramine to pentaethylene hexamine. Another preferred category of such acylating agents is comprised of at least one hydrocarbyl substituted succinic acylating agent in which the substituent is principally alkyl, alkenyl, or polyethylenically unsaturated alkenyl, or any combination thereof and wherein such substituent has an average of from 50 to 5000 carbon atoms. Particularly preferred for use as the acylating agent is (a) at least one polyisobutenyl substituted succinic acid or (b) at least one polyisobutenyl substituted succinic anhydride or (c) a combination of at least one polyisobutenyl substituted succinic acid and at least one polyisobutenyl substituted succinic anhydride in which the polyisobutenyl substituent in (a), (b) or (c) is derived from polyisobutene having a number average molecular weight in the range of 700 to 5,000.

As is well known, the substituted succinic acylating agents are those which can be characterized by the presence within their structure of two groups or moieties. The first group or moiety is a substituent group derived from a polyalkene. The polyalkene from which the substituted groups are derived is characterized by an M_n (number average molecular weight) value of typically from 500 to 10,000, and preferably in the range of from 700 to 5,000.

The second group or moiety is the succinic group, a group characterized by the structure



Formula I

wherein X and X' are the same or different provided at least one of X and X' is such that the substituted succinic acylating agent can function as a carboxylic acylating agent. In other words, at least one of X and X' must be such that the substituted acylating agent can esterify alcohols, form amides or amine salts with ammonia or amines, form metal salts with reactive metals or basically reacting metal compounds, and otherwise functions as a conventional carboxylic acid acylating agent. Transesterification and transamidation reactions are considered, for purposes of this invention, as conventional acylation reactions.

Thus, X and/or X' is usually -OH, -O-hydrocarbyl; -O-M⁺ where M⁺ represents one equivalent of a metal, ammonium or amine cation, -NH₂, -Cl, -Br, and together, X and X' can be -O- so as to form the anhydride.

Any of a variety of known procedures can be used to produce the substituted succinic acylating agents.

One procedure for preparing the substituted succinic acylating agents is illustrated, in part, by the two-step procedure described in U.S. Pat. No. 3,219,666.

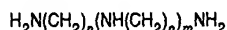
Another procedure for preparing substituted succinic acid acylating agents utilizes a process described in U.S. Pat. No. 3,912,764 and U.K. Pat. No. 1,440,219.

Other known processes for preparing the substituted succinic acylating agents include the one-step process described in U.S. Pat. Nos. 3,215,707 and 3,231,587.

Further details concerning procedures for producing the substituted acylating agents have been extensively described in the patent literature, such as for example in U.S. Pat. No. 4,234,435. Thus, further amplification of such procedures herein is deemed unnecessary.

The other principal reactant utilized in forming the succinimides which preferably are used in the process of this invention is one or a mixture of polyamines which preferably has at least one primary amino group in the molecule and which additionally contains an average of at least two other amino nitrogen atoms in the molecule. For best results, the polyamines should contain at least two primary amino groups in the molecule.

One preferred type of polyamines is comprised of alkylene polyamines such as those represented by the formula



wherein n is 2 to about 10 (preferably 2 to 4, more preferably 2 to 3, and most preferably 2) and m is 0 to 10, (preferably 1 to 6).

Particularly useful commercially-available mixtures of polyethylene polyamines are those having an overall average approximate composition falling in the range of triethylene tetramine to pentaethylene hexamine. Commercially-available mixtures of polyethylene polyamines often contain minor amounts of cyclic species such as aminoalkyl-substituted piperazines and the like.

In principle, any polyamine having at least one primary amino group and an average of at least three amino nitrogen atoms in the molecule can be used in forming the succinimide utilized in the practice of this invention. As noted above, product mixtures known in the trade as "triethylene tetramine", "tetraethylene pentamine", and "pentaethylene hexamine" are most preferred.

In forming the initial preferred succinimide used in the practice of this invention mole ratios of the hydrocarbyl substituted succinic acylating agent to polyamine reactant ranges from 1 : 1 to 4 : 1, and preferably from 1.5 : 1 to 3 : 1.

Dibasic Acylating Agent

A wide variety of dibasic acylating agents can be reacted with the basic nitrogen-containing ashless dispersant (e.g., succinimide, Mannich reaction product, succinic acid ester-amide, etc.) in the reaction of (i) above. The principal requirement is that such acylating agent contain at most 12 carbon atoms in the molecule, preferably up to 8 carbon atoms in the molecule, and more preferably up to 6 carbon atoms in the molecule. The most preferred acylating agents for use in reaction (i) contain 4 carbon atoms in the molecule. Thus use can be made of dibasic acids and anhydrides, esters and acyl halides thereof which contain a total of up to 12 carbon atoms in the molecule (excluding carbon atoms of an esterifying alcohol). Among such compounds are azelaic acid, adipic acid, succinic acid, lower alkyl-substituted succinic acid, succinic anhydride, lower alkyl-substituted succinic anhydride, glutaric acid, pimelic acid, suberic acid, sebacic acid, and like dibasic acids, anhydrides, acyl halides, and esters which contain (excluding carbon atoms of esterifying alcohols) up to 12 carbon atoms in the molecule. Preferred are maleic acid, maleic anhydride, fumaric acid and malic acid. Most preferred is maleic anhydride.

Phosphorus Compounds

The other reactant(s) with which the basic nitrogen-containing dispersant is reacted either before, during or subsequent to reaction with the above dibasic acylating agent and/or the ensuing boron compound(s) is a phosphorus compound or mixture of phosphorus compounds capable of introducing phosphorus-containing species into the ashless dispersant undergoing such reaction.

The following compounds are used phosphorous acid (H_3PO_3 , sometimes depicted as $H_2(HPO_3)$), and sometimes called ortho-phosphorus acid or phosphonic acid), hypophosphoric acid ($H_4P_2O_6$), metaphosphoric acid (HPO_3), pyrophosphoric acid ($H_4P_2O_7$), hypophosphorous acid (H_3PO_2 , sometimes called phosphinic acid), pyrophosphorous acid ($H_4P_2O_5$, sometimes called pyrophosphonic acid), phosphinous acid (H_3PO), tripolyphosphoric acid ($H_5P_3O_{10}$), tetrapolyphosphoric acid ($H_6P_4O_{13}$) and trimetaphosphoric acid ($H_3P_3O_9$).

Also used though less preferred, are the inorganic phosphorus halide compounds such as PCl_3 , PBr_3 and $PCOCl_3$. The preferred phosphorous reagent is phosphorous acid, (H_3PO_3).

Boron Compounds

The other reactant(s) with which the basic nitrogen-containing dispersant is reacted either before, during or subsequent to reaction with the above dibasic acylating agent and/or the above phosphorus reactant is a boron compound or mixtures of boron compounds capable of introducing boron-containing species into the ashless dispersant undergoing the reaction. Any boron compound, organic or inorganic, capable of undergoing such reaction can be used. Accordingly use can be made of boron oxide, boron oxide hydrate, boron trifluoride, boron tribromide, boron trichloride, HBF₄ boron acids such as boronic acid (e.g., alkyl-B(OH)₂ or aryl-B(OH)₂), boric acid, (i.e., H₃B₃), tetraboric acid (i.e., H₂B₅O₇), metaboric acid (i.e., HBO₂), ammonium salts of such boron acids, and esters of such boron acids. The use of complexes of a boron trihalide with ethers, organic acids, inorganic acids, or hydrocarbons is a convenient means of introducing the boron reactant into the reaction mixture. Such complexes are known and are exemplified by boron trifluoride-diethyl ether, boron trifluoride-phenol, boron trifluoride-phosphoric acid, boron trichloride-chloroacetic acid, boron tribromide-dioxane, and boron trifluoride-methyl ethyl ether.

Specific examples of boronic acids include methyl boronic acid, phenyl-boronic acid, cyclohexyl boronic acid, p-heptylphenyl boronic acid and dodecyl boronic acid.

The boron acid esters include especially mono, di-, and tri-organic esters of boric acid with alcohols or phenols such as, e.g., methanol, ethanol, isopropanol, cyclohexanol, cyclopentanol, 1-octanol, 2-octanol, dodecanol, behenyl alcohol, oleyl alcohol, stearyl alcohol, benzyl alcohol, 2-butyl cyclohexanol, ethylene glycol, propylene glycol, trimethylene glycol, 1,3-butanediol, 2,4-hexanediol, 1,2-cyclohexanediol, 1,3-octanediol, glycerol, pentaerythritol, diethylene glycol, carbitol, Cellosolve, triethylene glycol, tripropylene glycol, phenol, naphthol, p-butylphenol, o,p-diheptylphenol, n-cyclohexylphenol, 2,2-bis-(p-hydroxyphenyl)propane, polyisobutene (molecular weight of 1500)-substituted phenol, ethylene chlorohydrin, o-chlorophenol, m-nitrophenol, 6-bromo-octanol, m-nitrophenol, 6-bromo-octanol, m-nitrophenol, 6-bromo-octanol, and 7-keto-decanol. Lower alcohols, 1,2-glycols, and 1,3-glycols, i.e., those having less than about 8 carbon atoms are especially useful for preparing the boric acid esters for the purpose of this invention.

Reaction Conditions

In conducting the foregoing reactions, any temperature at which the desired reaction(s) occur at a satisfactory reaction rate can be used. Ordinarily, the acylation reaction between the basic nitrogen-containing dispersant (phosphorylated or non-phosphorylated and boronated or non-boronated) and the dibasic acylating agent is conducted at temperatures in the range of 80 to 200°C, more preferably 140 to 180°C. The phosphorylation reaction and the boronation reaction (whether conducted concurrently or separately) are likewise normally performed at temperatures within either of the foregoing ranges. However, departures from these ranges can be made whenever deemed necessary or desirable. These reactions may be conducted in the presence or absence of an ancillary diluent or liquid reaction medium, such as a mineral lubricating oil solvent. If the reaction is conducted in the absence of an ancillary solvent of this type, such is usually added to the reaction product on completion of the reaction. In this way the final product is in the form of a convenient solution in lubricating oil and thus is compatible with a lubricating oil base stock. Suitable solvent oils include lubricating oils having a viscosity (ASTM D 445) of 2 to 40, preferably 3 to 12 centistokes (cSt) at 100°C, with the primarily paraffinic mineral oils such as Solvent 100 Neutral being particularly preferred. Other types of lubricating oil base stocks can be used, such as synthetic lubricants including polyesters, poly- α -olefins, and the like. Blends of mineral oil and synthetic lubricating oils are also suitable for various applications in accordance with this invention.

The proportions of the reactants will to some extent be dependent on the nature of the basic-nitrogen containing dispersant being utilized, principally the content of basic nitrogen therein. Thus optimal proportions may, in some cases, be best defined by performing a few pilot experiments. Generally speaking, however, the dibasic acylating agent is employed in amounts ranging from 0.01 to 0.5 moles per average equivalent of nitrogen in the initial ashless dispersant (s), with the proviso that the resultant product contains at least 0.05 equivalent of basic nitrogen. Preferably the amount of dibasic acylating agent employed ranges from 0.02 to 0.3 moles per average equivalent of nitrogen in the initial ashless dispersant with the proviso that the resultant product contains at least 0.1 equivalent of basic nitrogen. In the case of use of a succinimide as the initial ashless dispersant, it is preferred to utilize an amount of the dibasic acylating agent such that the total mole ratio of (a) dibasic acylating agent plus (b) the aliphatic hydrocarbyl substituted succinic acylating agent used in forming the initial succinimide falls in the range of from 1.5 to 3.5 moles of (a) and (b) per mole of polyamine, more preferably 1.6 to 2.8 moles of (a) and (b) per mole of polyamine, and most preferably 1.6 to 2.2 moles of (a) and (b) per mole of polyamine. Here again, departures from such proportions may be utilized if found efficacious in any given situation.

In the case of the phosphorus reactant, the amounts used should be sufficient to introduce up to 5%, and preferably from 0.05 to 2.5% of phosphorus (expressed as weight % of elemental phosphorus) into the overall final co-reacted dispersant.

In the case of the boron reactant, the amounts used should be sufficient to introduce up to 5%, and preferably from 0.05 to 2.5% of boron (expressed as weight % of elemental boron) into the overall final co-reacted dispersant.

It will be understood of course that in any given case the amount of dibasic acylating agent, phosphorus compound and boron compound used should be sufficient to provide a product having both satisfactory fluoroelastomer compatibility and adequate dispersancy performance.

Modified Processing

As noted above, the dispersants of this invention are formed by subjecting a basic nitrogen-containing ashless dispersant to three reactions, namely, acylation with at least one dibasic acylating agent, phosphorylation with at least one phosphorylation reagent, and boronation with at least one boronation reagent. Ordinarily these reactions will be conducted either concurrently or in sequence. It is, of course, not necessary that these reactions be conducted in the same plant or at periods of time proximate to each other. For example, in one embodiment of this invention, a phosphorylated basic nitrogen-containing ashless dispersant from one manufacturer need only be subjected to acylation with a dibasic acylating agent of the type described hereinabove and to boronation with a boronating agent of the type described hereinabove in order to produce a novel phosphorylated-acylated-boronated ashless dispersant of this invention. Likewise, one may procure a suitable acylated basic nitrogen-containing ashless dispersant from a given supplier (i.e., a basic nitrogen-containing ashless dispersant which has been subjected to acylation with a dibasic acylating agent of the type described hereinabove) and subject the same to phosphorylation and boronation in order to produce a novel acylated-phosphorylated-boronated ashless dispersant of this invention. Similarly one may procure a suitable boronated basic nitrogen-containing ashless dispersant from a given supplier and subject the same to acylation and phosphorylation in accordance with the procedures described herein to thereby produce a novel boronated-acylated-phosphorylated ashless dispersant of this invention. In short, the novel products of this invention can be produced in accordance with this invention by two or more distinct and separate parties, if desired.

Although it is preferred to use separate and distinct phosphorus compounds and boron compounds in effecting the phosphorylation and boronation reactions, it is possible to employ compounds which contain both phosphorus and boron in the molecule such as borophosphates, etc., in order to concurrently phosphorylate and boronate the ashless dispersant.

Further Treatments

Although ordinarily unnecessary, the acylated, phosphorylated, boronated ashless dispersants of this invention can be reacted with one or more additional treating agents, either before, during or after any of the above-referred-to acylation, phosphorylation and boronation reactions. Treating agents used for this purpose include, for example, carbon disulphide, hydrogen sulphide, sulphur, sulphur chloride, alkenyl cyanides, mono-, tri-, tetra-, etc. carboxylic acid acylating agents, aldehyde, ketones, urea, thiourea, guanidine, dicyanodiamide, hydrocarbyl thiocyanates, hydrocarbyl isocyanates, hydrocarbyl isothiocyanates, epoxides, episulphides, formaldehyde or formaldehyde producing compounds plus phenols, sulphur plus phenols, and many others.

Since treating processes involving numerous treating reagents are known as regards treatment of various ashless dispersants, further details concerning such technology are readily available in the literature.

Uses

The novel compositions of this invention can be used as ashless dispersants in a wide variety of oleaginous fluids and as detergents or deposit reducers in hydrocarbonaceous fuels such as gasoline, diesel fuel, kerosene, burner fuel, gas oil, jet fuel, turbine fuel, and the like. They can be used in lubricating oil and functional fluid compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, cutting oils, etc. The lubricant may be a mineral oil, a synthetic oil, a natural oil such as a vegetable oil, or a mixture thereof.

Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid α -olefin polymers of appropriate viscosity. Especially useful are hydrogenated or unhydrogenated liquid oligomers of C_6 - C_{16} α -olefins, such as hydrogenated or unhydrogenated α -decene trimer. Alkyl benzenes of appropriate viscosity can also be used. Useful synthetic esters include the esters of monocarboxylic and polycarboxylic acids with monohydroxy alcohols and polyols.

Complex esters made from mixtures of mono- and di-carboxylic acids and mono- and/or polyhydric alkanols can also be used.

Typical natural oils that may be used include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such oils may be partially or fully hydrogenated, if desired.

Viscosity index improvers may be included in the mineral, synthetic and natural oils (or any blends thereof) in order to achieve the viscosity properties deemed necessary or desirable.

The finished lubricating oil compositions and additive concentrates of this invention containing the present ashless dispersant systems will usually also contain other well-known additives in order to partake of their special properties.

5 Among the numerous additives which can be employed in the lubricants and functional fluids and additive concentrates of this invention are those of the types described hereinafter.

The lubricants and functional fluids of this invention are of particular utility in applications wherein the oil of lubricating viscosity comes in contact with fluor elastomers. In such applications, the compatibility of the lubricant or functional fluid of this invention so utilized, is significantly enhanced as compared to the corresponding lubricant or functional fluid containing the corresponding untreated basic nitrogen-containing ashless dispersant.

10 The concentrations of the ashless dispersants of this invention in oleaginous fluids will generally fall in the range of up to about 10 weight percent, for example 1 to 9 weight percent. When used in fuel compositions, amounts of up to about 5 weight percent are typical.

The following examples, in which all parts and percentages are by weight, illustrate, but do not limit, and should not be construed as limiting, the practice of this invention.

EXAMPLE 1

In a first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) formed from polyisobutylene (number average molecular weight \approx 1300) and tetraethylene pentamine (TEPA) in a mole ratio of 1.8:1 were reacted at 165-170°C for 4 hours. In a second stage reaction, maleic anhydride (MA) was added to the first stage reaction product in amount equivalent to 0.35 mole per mole of TEPA used in the first stage and the resultant mixture was heated at 165-170°C for 1.5 hours after which oil was added. In a third stage reaction, boric acid followed by H_3PO_3 was added to the second stage reaction mixture at a temperature of 105°C in amounts corresponding to 1.6 and 1.21 moles respectively per mole of TEPA initially employed. The mixture was stirred at 105°C for two hours and then heated to 155°C and a vacuum of 40 mm applied to remove water formed in the third stage reaction. The resulting succinimide is acylated, phosphorylated, and boronated, and had a nitrogen content of 1.75%, a phosphorus content of 1.02%, and a boron content of 0.43%.

EXAMPLE 2

The procedure of Example 1 was repeated except that the amount of H_3PO_3 was reduced to 0.6 moles per mole of TEPA initially used. The final product, diluted to 1.74% nitrogen content with 100 solvent neutral mineral oil contains 0.40% phosphorus and 0.49% boron.

EXAMPLE 3

Repetition of Example 1 wherein the amount of H_3PO_3 was still further reduced to 0.3 moles per mole of TEPA initially used yielded a concentrate (diluted as in Example 1) having a phosphorus content of 0.23% and a boron content of 0.40%.

EXAMPLE 4

45 Example 1 was repeated but the boric acid and phosphorus acid were added at 155°C instead of 105°C. After stirring for two hours the mixture was stripped as before. The product concentrate (diluted as in Example 1) contains 1.05% phosphorus and 0.45% boron.

EXAMPLE 5

50 The procedure of Example 1 is repeated except that the reaction with the boric acid and phosphorous acid is conducted before the reaction with maleic anhydride and the amounts used correspond to 1.6 and 1.21 moles respectively per mole of TEPA used in the first stage reaction. The final product (diluted as in Example 1) contains 0.40% phosphorus, 0.97% boron and 1.76% nitrogen.

EXAMPLE 6

Example 5 is repeated except that the maleic anhydride, boric acid, and phosphorous acid are concurrently reacted with the succinimide formed in the first stage reaction. One such product on dilution with 100 solvent neutral mineral

oil contained 1.74% nitrogen and 0.34% phosphorus.

EXAMPLE 7

In the first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) formed from polyisobutylene (number average molecular weight = 1300) and tetraethylene pentamine (TEPA) in a mole ratio of 1.8:1 were reacted at 165-170°C for 4 hours and then mineral oil added. In a second stage reaction, maleic anhydride (MA) was added to the first stage reaction product in an amount equivalent to 0.14 moles per mole of TEPA used in the first stage and the resultant mixture was heated at 165-170°C for 1 1/2 hours. The temperature was reduced to 150°C and boric acid (2.2 moles per mole of TEPA) was added. After stirring for 30 minutes, phosphorous acid (0.5 moles per mole of TEPA) was added and the mixture stirred for a further 30 minutes. A vacuum of 40 mm of Hg was then applied and the mixture stripped for 1 1/2 hours. A further charge of mineral oil is then made and the product filtered to give an additive concentrate with a nitrogen content of 1.51%, a phosphorus content of 0.20%, and a boron content of 0.56%.

EXAMPLE 8

The procedure of Example 7 is repeated except that in the third stage, the amount of H_3PO_3 is reduced to 0.25 moles per mole of TEPA used in the first stage reaction. The product on dilution has a nitrogen content of 1.46% and a phosphorus content of 0.20%, and a boron content of 0.63%.

EXAMPLE 9

In the first stage reaction, polyisobutenylsuccinic anhydride (PIBSA) (number average molecular weight = 1300) and TETA are reacted in a mole ratio of 2.0:1. In a second stage, maleic anhydride is added to the first stage reaction product in an amount equivalent to 0.30 mole per mole of TETA used in the first stage and the resultant mixture is heated at 165-170°C for 1 1/2 hours after which mineral oil is added. In a third stage reaction, boric acid and phosphorous acid are added to the second stage reaction product in amounts equivalent to 1.0 moles per mole of TETA used in the first stage and the resultant mixture is heated at 150-155°C for 3 hours. The product has a nitrogen content of 1.45% and a phosphorus content of 0.80%, and a boron content of 0.25%.

In order to determine the compatibility of various succinimide dispersants with fluoroelastomers, a series of finished crankcase lubricating oils for use in internal combustion engines containing various substituted succinimide dispersants were formulated. Each such oil contained, in addition to the succinimide dispersant, conventional amounts of overbased sulphonates, zinc dialkyl dithiophosphate, antioxidant, viscosity index improver, rust inhibitor, and antifoam agent to provide an SAE 15W/40 crankcase lubricant-oil. The respective lubricants containing the succinimide dispersants of Examples 1-4 and 7-8 each contained an amount of such dispersant to provide a nitrogen content of 0.10%.

The resultant finished lubricating oils were subjected to the Volkswagen P.VW 3334 Elastomer Compatibility Test. The results wherein VITON AK6 fluoroelastomer was used are summarized in Table 1.

Table 1 -

Results of Fluoroelastomer Seal Tests			
Succinimide Used	Change in Elongation to Break Compared to Fresh Seal, %	Change in Tensile Strength Compared to Fresh Seal, %	Cracking Observed
Example 1	-8	-11	None
Example 2	-24	-22	None
Example 3	-24	-36	None
Example 4	-19	-18	None
Example 7	-30	-26	None
Example 8	-22	-22	None

In contrast, a corresponding untreated succinimide gives results in the above test in the order of -45% elongation change, -58% tensile strength change and it exhibits cracking.

Another feature of this invention is that the combined acylating, phosphorylation and boronation reactions, whether run serially in any order or concurrently, can yield products having lower viscosities and consequent improved handleability as compared to corresponding products formed using either acylation or boronation only. For example a succinimide formed as in the first stage of Example 1 and boronated with boric acid to a level of 1.6% boron (1.8% nitrogen) has a viscosity of approximately 2900 cSt at 100°C. A product formed by reacting PIBSA with TEPA and thereafter

reacting the succinimide with maleic anhydride (MA) (mole ratios of PIBSA : TEPA : MA = 2.05 : 1 : 1 (1.8% nitrogen) has a viscosity of 4500 cSt at 100°C. But a product of this invention formed from PIBSA, TEPA and MA (mole ratio: 1.8 : 1 : 0.3 respectively) and with a phosphorus content of 1.05% and boron content of 0.45% (1.8% nitrogen) had a viscosity at 100°C of approximately 2160 cSt.

5 Additive concentrates of this invention generally contain 10 to 95 weight percent of one or more ashless dispersants of this invention, 0 to 90 weight percent liquid diluent and 0 to 90 weight percent of other additives commonly employed in lubricants and functional fluids.

The dispersants utilized according to the invention can be incorporated in a wide variety of lubricants. They can be used in lubricating oil compositions, such as automotive crankcase lubricating oils, automatic transmission fluids, or gear oils in effective amounts to provide active ingredient concentrations in finished formulations generally within 10 the range of 0.5 to 10 weight percent, for example, 1 to 9 weight percent, preferably 2 to 8 weight percent, of the total composition. Conventionally, the dispersants are admixed with the lubricating oils as dispersant solution concentrates which usually contain up to about 50 weight percent of the active ingredient additive compound dissolved in mineral oil, preferably a mineral oil having an ASTM D-445 viscosity of 2 to 40, preferably 3 to 12 centistokes at 100°C. The 15 lubricating oil not only can be hydrocarbon oils of lubricating viscosity derived from petroleum but also can be natural oils of suitable viscosities such as rapeseed oil, etc., and synthetic lubricating oils such as hydrogenated polyolefin oils; poly- α -olefins (e.g., hydrogenated or unhydrogenated α -olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; and mixtures of lubricating oils and synthetic oils in any 20 proportion. The term "lubricating oil" for this disclosure includes all the foregoing. The useful dispersant may be conveniently dispersed as a concentrate of 10 to 80 weight percent of mineral oil, e.g., Solvent 100 Neutral oil with or without other additives being present and such concentrates are a further embodiment of this invention.

Other additives which may be included in the lubricants, functional fluids and additive concentrates of this invention include such substances as zinc dialkyl (C_3 - C_{10}), dicycloalkyl (C_6 - C_{20}), and/or diaryl (C_6 - C_{20}) dithiophosphate wear 25 inhibitors, generally present in amounts of about 0.5 to 5 weight percent. Useful detergents include the oil-soluble normal basic or overbased metal, e.g., calcium, magnesium, barium, etc., salts of petroleum naphthenic acids, petroleum sulfonic acids, alkyl benzene sulfonic acids, oil-soluble fatty acids, alkyl salicylic acids, sulphurized or unsulphurized alkyl phenates, and hydrolysed or unhydrolysed phosphosulphurized polyolefins. Gasoline engine crankcase lubricants typically contain, for example, from 0.5 to 5 weight percent of one or more detergent additives. Diesel engine 30 crankcase oils may contain substantially higher levels of detergent additives. Preferred detergents are the calcium and magnesium normal or overbased phenates, sulphurized phenates or sulfonates.

Pour point depressants which may be present in amounts of from 0.01 to 1 weight percent in the lubricant or functional fluid include wax alkylated aromatic hydrocarbons, olefin polymers and copolymers, and acrylate and methacrylate polymers and copolymers.

35 Viscosity index improvers, the concentrations of which may vary in the lubricants from 0.2 to 15 weight percent, (preferably from 0.5 to 5 weight percent) depending on the viscosity grade required, include hydrocarbon polymers grafted with, for example, nitrogen-containing monomers, olefin polymers such as polybutene, ethylene-propylene copolymers, hydrogenated polymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate, post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, styrene/maleic anhydride polymers 40 post-treated with alcohols and amines, etc.

Antiwear activity can be provided by 0.01 to 2 weight percent in the oil of the aforementioned metal dihydrocarbyl dithiophosphates and the corresponding precursor esters, phosphosulphurized pinenes, sulphurized olefins and hydrocarbons, sulphurized fatty esters and alkyl polysulphides. Preferred are the zinc dihydrocarbyl dithiophosphates 45 which are salts of dihydrocarbyl esters of dithiophosphoric acids.

Other additives include effective amounts of friction modifiers or fuel economy additives such as the alkyl phosphonates as disclosed in U.S. 4,356,097, aliphatic hydrocarbyl substituted succinimides as disclosed in EPO 0020037, dimer acid esters, as disclosed in U.S. 4,105,571, oleamide, etc., which are present in the oil in amounts of 0.1 to 5 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 0.2 weight percent based on the weight of the formulated oil.

50 Antioxidants are also usually employed in the additive concentrates and lubricants and functional fluids of this invention. Preferred are hindered phenolic antioxidants, methylene bridged alkylphenols, secondary aromatic amines, sulphurized phenols, alkyl phenothiazines, substituted triazines and ureas, and copper compounds such as copper naphthenate and copper oleate, among others. Typically the oil of lubricating viscosity will contain 0.001 to 2.5 weight percent of antioxidant. Particularly preferred are combinations of (i) at least one oil-soluble mononuclear monohydric 55 phenol having a tertiary alkyl group in at least one position ortho to the hydroxyl group and a hydrogen atom or a tertiary alkyl group in the position para to the hydroxyl group, (ii) at least one oil-soluble methylene-bridged tertiary alkyl-

substituted polyphenol, and (iii) at least one oil-soluble aromatic secondary amine, the proportions of (i), (ii) and (iii) being such that the weight percentage of nitrogen in component (iii) relative to the total weight of components (i), (ii) and (iii) is in the range of 0.05% to 1.5%, and the weight ratio of monohydric phenols:methylene-bridged polyphenols in the composition is in the range of 15:1 to 1:2. Preferably component (i) in the foregoing composition is an oil-soluble mixture of said mononuclear monohydric phenols. It is likewise preferred that component (ii) of the foregoing composition be an oil-soluble mixture of said methylene-bridged tertiary alkyl-substituted phenols.

Particularly preferred is an antioxidant composition which comprises a combination of (i) an oil soluble mixture of sterically-hindered tertiary alkylated monohydric phenols, (ii) an oil-soluble mixture of sterically-hindered tertiary alkylated methylene-bridged polyphenols, and (iii) at least one oil-soluble aromatic secondary amine, the proportions of (i), (ii) and (iii) being such that the weight percentage of nitrogen in component (iii) relative to the total weight of components (i), (ii) and (iii) is in the range of 0.05% to 1.5%, preferably in the range of 0.1% to 0.8%, and most preferably in the range of 0.3% to 0.7%, and the weight ratio of monohydric phenols:methylene-bridged polyphenols in the composition is in the range of 15:1 to 1:2, preferably in the range of 10:1 to 1:1, and most preferably in the range of 5:1 to 1:1. Preferred secondary aromatic amines are alkyl diphenylamines containing 1 or 2 alkyl substituents each having up to about 16 carbon atoms, phenyl- α -naphthylamine, phenyl- β -naphthylamine, alkyl- or aralkyl-substituted phenyl- α -naphthylamine containing 1 or 2 alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl- β -naphthylamine containing 1 or 2 alkyl or aralkyl groups each having up to about 16 carbon atoms, and similar compounds. One such preferred compound is available commercially as Nugalube 438L, a material which is understood to be predominantly a 4,4'-dinonyldiphenylamine (i.e., bis(4-nonylphenyl)amine) wherein the nonyl groups are branched.

Other well known components such as rust inhibitors, wax modifiers, foam inhibitors, copper passivators, sulphur scavengers, seal swell agents, color stabilizers, and like materials can be included in the compositions of this invention, provided of course that they are compatible with the ashless dispersant of this invention and the other component or components being employed.

This invention also includes among its embodiments improved methods of lubricating mechanical parts in the presence of at least one fluoroelastomer surface. In the practice of such methods, the lubrication is effected by means of a lubricating oil or functional fluid containing an ashless dispersant of this invention. The practice of such methods results in a lower -- oftentimes a substantially lower -- amount of degradation of the fluoroelastomer contacted by the lubricating oil or functional fluid containing such ashless dispersant as compared to the amount of degradation that would occur under the same conditions using the same oil or fluid composition containing the same total quantity of the corresponding initial untreated ashless dispersant.

Mechanical mechanisms and systems which may be lubricated include crankcases of internal combustion engines; vehicular transmissions; hydraulic systems; hypoid axles; mechanical steering drives in passenger cars, in trucks, and in cross-country vehicles; planetary hub reduction axles and transfer gear boxes in utility vehicles such as trucks; pinion hub reduction gear boxes; synchromesh and synchronizer type gear boxes; power take-off gears; and limited slip rear axles. The ashless dispersant can also be utilized in metal working, machining, and cutting oils such as are applied to work pieces during cutting and shaping operations.

40 Claims

1. An oil soluble dispersant composition formable by reacting concurrently or sequentially in any order, a basic nitrogen-containing ashless dispersant (i) with at least one dibasic acylating agent containing up to 12 carbon atoms per molecule, (ii) with at least one phosphorylating compound selected from phosphorous acid, hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid, hypophosphorous acid, pyrophosphorous acid, phosphinous acid, tripolyphosphoric acid, tetrapolyphosphoric acid, trimetaphosphoric acid, POCl_3 , PCl_3 and PBr_3 , and (iii) with at least one boronating compound.
2. A composition according to claim 1, wherein reaction (i) is conducted prior to reactions (ii) and (iii).
3. A composition according to claim 1, wherein reactions (ii) and (iii) are conducted prior to reaction (i).
4. A composition according to claim 1, wherein reactions (i), (ii) and (iii) are conducted concurrently.
5. A composition according to any one of claims 1 to 4, wherein the reaction (ii) is conducted using phosphorous acid; and reaction (iii) is conducted using (a) at least one boron acid or anhydride or ester thereof, or (b) any combination thereof.

6. A composition according to any one of the preceding claims, wherein the acylating agent used in reaction (i) is maleic anhydride, maleic acid, fumaric acid, malic acid or any combination thereof.
7. A composition according to any one of the preceding claims, wherein the basic nitrogen-containing ashless dispersant is a succinimide dispersant having an average of at least 3 nitrogen atoms per molecule.
8. A composition according to any one of the preceding claims, wherein the basic nitrogen-containing ashless dispersant is a succinimide dispersant formed from an alkyl or alkenyl succinic acylating agent having an average of at least 40 carbon atoms in the alkyl or alkenyl group and an alkylene polyamine mixture having an average of at least 3 nitrogen atoms per molecule.
9. A composition according to any of the preceding claims, wherein the basic nitrogen-containing ashless dispersant is a succinimide dispersant formed from a polyisobutenyl succinic acylating agent derived from polyisobutene having a number average molecular weight in the range of 500 to 10,000 and an ethylene polyamine mixture including cyclic and acyclic structures, said mixture having an average overall composition approximating to a mixture in the range of from triethylene tetramine to pentaethylene hexamine.
10. A composition according to any one of the preceding claims, wherein the dibasic acylating agent(s) is/are employed in amounts ranging from 0.01 to 0.5 moles per average equivalent of nitrogen in the basic nitrogen-containing ashless dispersant(s), with the proviso that the resultant product contains at least 0.05 equivalent of basic nitrogen, and wherein up to about 5% of phosphorus expressed as weight % of elemental phosphorus, and up to about 5% of boron, expressed as weight % of elemental boron, are introduced into the overall final co-reacted dispersant.
11. A composition according to any one of claims 8 to 10, wherein the dibasic acylating agent(s) is/are employed in amounts such that the total mole ratio of (a) dibasic acylating plus (b) the alkenyl succinic acylating agent used in forming the initial succinimide falls in the range of from 1.5 to 3.5 moles of (a) and (b) per mole of polyamine; and wherein from 0.05 to 2.5% of phosphorus, expressed as weight % of elemental phosphorus, and from 0.05% to 2.5% of boron, expressed as weight % of elemental boron, are introduced into the overall final co-reacted dispersant.
12. A lubricating oil or functional fluid composition comprising a major proportion of an oil of lubricating viscosity and a minor dispersant amount of a dispersant composition as defined in any one of claims 1 to 11.
13. An additive concentrate containing a dispersant composition as defined in any one of claims 1 to 11.
14. A process for preparing an oil soluble dispersant composition as defined in claim 1, which comprises
 - (a) reacting a basic nitrogen-containing ashless dispersant with at least one dibasic acylating agent having up to 12 carbon atoms in the molecule, with at least one phosphorylating compound selected from phosphorous acid, hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid, hypophosphorous acid, pyrophosphorous acid, phosphinous acid, tripolyphosphoric acid, tetrapolyphosphoric acid, trimetaphosphoric acid, POCl_3 , PCl_3 and PBr_3 , and with at least one boronating compound, such reactions being conducted concurrently or sequentially in any order;
 - (b) reacting a basic nitrogen-containing dispersant phosphorylated with at least one phosphorylating compound selected from phosphorous acid, hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid, hypophosphorous acid, pyrophosphorous acid, phosphinous acid, tripolyphosphoric acid, tetrapolyphosphoric acid, trimetaphosphoric acid, POCl_3 , PCl_3 and PBr_3 with a dibasic acylating agent having up to 12 carbon atoms in the molecule and with at least one boronating compound;
 - (c) reacting a basic nitrogen-containing ashless dispersant acylated with a dibasic acylating agent having up to 12 carbon atoms in the molecule with at least one phosphorylating compound selected from phosphorous acid, hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid, hypophosphorous acid, pyrophosphorous acid, phosphinous acid, tripolyphosphoric acid, tetrapolyphosphoric acid, trimetaphosphoric acid, POCl_3 , PCl_3 and PBr_3 and with at least one boronating compound; or
 - (d) reacting a boronated basic nitrogen-containing dispersant with a dibasic acylating agent having up to 12 carbon atoms in the molecule and with at least one phosphorylating compound selected from phosphorous acid, hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid, hypophosphorous acid, pyrophosphorous acid, phosphinous acid, tripolyphosphoric acid, tetrapolyphosphoric acid, trimetaphosphoric acid, POCl_3 , PCl_3 and PBr_3 .

EP 0 537 387 B1

15. A process according to claim 14, wherein the basic nitrogen-containing dispersant subjected to the process is a succinimide dispersant formed from an alkyl or alkenyl succinic acylating agent having an average of at least 40 carbon atoms in the alkyl or alkenyl group and an alkylene polyamine mixture having an average of at least 3 nitrogen atoms per molecule.

16. A process according to claim 14, wherein the initial basic nitrogen-containing dispersant is a succinimide dispersant formed from a polyisobutyl succinic acylating agent derived from polyisobutene having a number average molecular weight in the range of 500 to 10,000 and an ethylene polyamine mixture including cyclic and acyclic structures, said mixture having an average overall composition approximating a mixture in the range of from triethylene tetramine to pentaethylene hexamine.

17. A method of lubricating mechanical parts in which a fluoroelastomer surface is in contact with a lubricant or functional fluid, which method is effected by means of a lubricating oil or functional fluid comprising a dispersant composition as defined in any one of claims 1 to 11.

Patentansprüche

1. Öllösliche Dispergiemittelzusammensetzung, die durch gleichzeitige oder aufeinanderfolgende Umsetzung in beliebiger Reihenfolge eines basischen Stickstoff enthaltenden aschefreien Dispergiemittels (i) mit mindestens einem dibasischen, bis zu 12 Kohlenstoffatome pro Molekül enthaltenden Acylierungsmittel, (ii) mit mindestens einer aus Phosphorigsäure, Hypophosphorsäure, Metaphosphorsäure, Pyrophosphorsäure, Hypophosphorigsäure, Pyrophosphorigsäure, Phosphinigsäure, Triphosphorsäure, Tetraphosphorsäure, Trimetaphosphorsäure, POCl₃, PCl₃ und PBr₃ ausgewählten phosphorylierenden Verbindung und (iii) mindestens einer borierenden Verbindung hergestellt werden kann.

2. Zusammensetzung nach Anspruch 1, in der die Reaktion (i) vor den Reaktionen (ii) und (iii) durchgeführt wird.

3. Zusammensetzung nach Anspruch 1, in der die Reaktionen (ii) und (iii) vor der Reaktion (i) durchgeführt werden.

4. Zusammensetzung nach Anspruch 1, in der die Reaktionen (i), (ii) und (iii) gleichzeitig durchgeführt werden.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, in der die Reaktion (ii) unter Verwendung von Phosphorigsäure und die Reaktion (iii) unter Verwendung von (a) mindestens einer Borsäure oder eines Anhydrids oder Esters davon oder (b) einer beliebigen Kombination davon durchgeführt wird.

6. Zusammensetzung nach einem der vorstehenden Ansprüche, in der das in der Reaktion (i) verwendete Acylierungsmittel Maleinsäureanhydrid, Maleinsäure, Fumarsäure, Äpfelsäure oder eine beliebige Kombination davon ist.

7. Zusammensetzung nach einem der vorstehenden Ansprüche, in der das basischen Stickstoff enthaltende aschefreie Dispergiemittel ein Succinimiddispergiemittel mit durchschnittlich mindestens 3 Stickstoffatomen pro Molekül ist.

8. Zusammensetzung nach einem der vorstehenden Ansprüche, in der das basischen Stickstoff enthaltende aschefreie Dispergiemittel ein Succinimiddispergiemittel ist, das aus einem Alkyl- oder Alkenylbernsteinsäure-Acylierungsmittel mit durchschnittlich mindestens 40 Kohlenstoffatomen in der Alkyl- oder Alkenylgruppe und einer Alkylpolyaminmischung mit durchschnittlich mindestens 3 Stickstoffatomen pro Molekül hergestellt wurde.

9. Zusammensetzung nach einem der vorstehenden Ansprüche, in der das basischen Stickstoff enthaltende aschefreie Dispergiemittel ein Succinimiddispergiemittel ist, das aus einem von Polyisobuten mit einem zahlenmittleren Molekulargewicht im Bereich von 500 bis 10.000 abgeleiteten Polyisobutenylbernsteinsäure-Acylierungsmittel und einer Ethylenpolyaminmischung einschließlich cyclischer und acyclischer Strukturen hergestellt wurde, wobei diese Mischung eine durchschnittliche Gesamtzusammensetzung aufweist, die einer Mischung im Bereich von Triäthyltetramin bis Pentaäthylenhexamin nahe kommt.

10. Zusammensetzung nach einem der vorstehenden Ansprüche, in der das oder die dibasischen Acylierungsmittel in Mengen von 0,01 bis 0,5 Mol pro durchschnittlichem Stickstoffäquivalent in dem oder den basischen Stickstoff

enthaltenden aschefreien Dispergiemitteln verwendet werden, mit der Maßgabe, daß das dabei entstehende Produkt mindestens 0,05 Äquivalente basischen Stickstoff enthält, wobei bis zu etwa 5 % Phosphor, ausgedrückt als Gew.-% elementaren Phosphors, und bis zu etwa 5 % Bor, ausgedrückt als Gew.-% elementaren Bors, in das fertige, gemeinsam umgesetzte Gesamtdispergiemittel eingebracht werden.

- 5 11. Zusammensetzung nach einem der Ansprüche 8 bis 10, in der das oder die dibasischen Acylierungsmittel in einer solchen Menge eingesetzt werden, daß das Gesamtmolverhältnis von (a) dibasischem Acylierungsmittel plus (b) dem zur Herstellung des Ausgangssuccinimids verwendeten Alkenylbernsteinsäure-Acylierungsmittel in den Bereich von 1,5 bis 3,5 Mol (a) und (b) pro Mol Polyamin fällt, und in der 0,05 bis 2,5 % Phosphor, ausgedrückt als Gew.-% elementaren Phosphors, und 0,05 bis 2,5 % Bor, ausgedrückt als Gew.-% elementaren Bors, in das fertige gemeinsam umgesetzte Gesamtdispergiemittel eingebracht werden.
- 10 12. Schmieröl oder funktionelle Fluidzusammensetzung, die einen größeren Anteil eines Öls von Schmierviskosität und eine kleinere dispergierend wirkende Menge einer Dispergiemittelzusammensetzung nach einem der Ansprüche 1 bis 11 enthält.
- 15 13. Additivkonzentrat, das eine Dispergiemittelzusammensetzung nach Anspruch 1, bei dem man
- 20 14. Verfahren zur Herstellung einer öllöslichen Dispergiemittelzusammensetzung nach Anspruch 1, bei dem man
 - (a) ein basischen Stickstoff enthaltendes aschefreies Dispergiemittel mit mindestens einem dibasischen Acylierungsmittel mit bis zu 12 Kohlenstoffatomen pro Molekül, mindestens einer aus Phosphorigsäure, Hypophosphorigsäure, Pyrophosphorigsäure, Pyrophosphorsäure, Metaphosphorsäure, Tetrapolyphosphorsäure, Trimetaphosphorsäure, POCl_3 , PCl_3 und Phosphinigsäure, Tripolyphosphorsäure, Tetrapolyphosphorsäure, Trimetaphosphorsäure, POCl_3 , PCl_3 und PBr_3 ausgewählten phosphorylierenden Verbindung und mindestens einer borierenden Verbindung zur Umsetzung bringt, wobei diese Reaktionen gleichzeitig oder nacheinander in beliebiger Reihenfolge durchgeführt werden können;
 - 25 (b) ein basischen Stickstoff enthaltendes, mit mindestens einer aus Phosphorigsäure, Hypophosphorsäure, Metaphosphorsäure, Pyrophosphorsäure, Hypophosphorigsäure, Pyrophosphorigsäure, Phosphinigsäure, Tripolyphosphorsäure, Tetrapolyphosphorsäure, Trimetaphosphorsäure, POCl_3 , PCl_3 und PBr_3 ausgewählten phosphorylierenden Verbindung phosphoryliertes Dispergiemittel mit einem dibasischen Acylierungsmittel mit bis zu 12 Kohlenstoffatomen im Molekül und mindestens einer borierenden Verbindung zur Umsetzung bringt;
 - 30 (c) ein basischen Stickstoff enthaltendes, mit einem dibasischen Acylierungsmittel mit bis zu 12 Kohlenstoffatomen im Molekül acyliertes aschefreies Dispergiemittel mit mindestens einer aus Phosphorigsäure, Hypophosphorsäure, Metaphosphorsäure, Pyrophosphorsäure, Hypophosphorigsäure, Pyrophosphorigsäure, Phosphinigsäure, Tripolyphosphorsäure, Tetrapolyphosphorsäure, Trimetaphosphorsäure, POCl_3 , PCl_3 und PBr_3 ausgewählten phosphorylierenden Verbindung und mindestens einer borierenden Verbindung zur Umsetzung bringt, oder
 - 35 (d) ein boriertes, basischen Stickstoff enthaltendes Dispergiemittel mit einem dibasischen Acylierungsmittel mit bis zu 12 Kohlenstoffatomen im Molekül und mindestens einer aus Phosphorigsäure, Hypophosphorsäure, Metaphosphorsäure, Pyrophosphorsäure, Hypophosphorigsäure, Pyrophosphorigsäure, Phosphinigsäure, Tripolyphosphorsäure, Tetrapolyphosphorsäure, Trimetaphosphorsäure, POCl_3 , PCl_3 und PBr_3 ausgewählten phosphorylierenden Verbindung zur Umsetzung bringt.
 - 40
 - 45
- 50 15. Verfahren nach Anspruch 14, bei dem das dem Verfahren unterzogene basischen Stickstoff enthaltende Dispergiemittel ein Succinimiddispergiemittel ist, das aus einem Alkyl- oder Alkenylbernsteinsäure-Acylierungsmittel mit durchschnittlich mindestens 40 Kohlenstoffatomen in der Alkyl- oder Alkenylgruppe und einer Alkylpolyaminmischung mit durchschnittlich mindestens 3 Stickstoffatomen pro Molekül hergestellt wurde.
- 55 16. Verfahren nach Anspruch 14, bei dem das als Ausgangsmaterial verwendete, basischen Stickstoff enthaltende aschefreie Dispergiemittel ein Succinimiddispergiemittel ist, das aus einem von Polyisobuten mit einem zahlenmittleren Molekulargewicht im Bereich von 500 bis 10.000 abgeleiteten Polyisobutenylbernsteinsäure-Acylierungsmittel und einer Ethylenpolyaminmischung einschließlich cyclischer und acyclischer Strukturen hergestellt wurde, wobei diese Mischung eine durchschnittliche Gesamtzusammensetzung aufweist, die einer Mischung im Bereich

von Triäthylentetramin bis Pentaäthylenhexamin nahe kommt.

17. Verfahren zum Schmieren mechanischer Teile, bei dem eine Fluorelastomeroberfläche in Kontakt mit einem Schmiermittel oder funktionellen Fluid kommt, wobei das Verfahren mittels eines Schmieröls oder funktionellen Fluids durchgeführt wird, das eine Dispergierrmittelzusammensetzung nach einem der Ansprüche 1 bis 11 enthält.

Revendications

1. Composition de dispersant, soluble dans l'huile, pouvant être préparée en faisant réagir conjointement ou successivement dans n'importe quel ordre un dispersant sans cendre azoté basique (i) avec au moins un agent diacide d'acylation contenant jusqu'à 12 atomes de carbone par molécule, (ii) avec au moins un composé de phosphorylation choisi entre l'acide phosphoreux, l'acide hypophosphorique, l'acide métaphosphorique, l'acide pyrophosphorique, l'acide hypophosphoreux, l'acide pyrophosphoreux, l'acide phosphineux, l'acide tripolyphosphorique, l'acide tétrapolyphosphorique, l'acide trimétaphosphorique, POCl_3 , PCl_3 et PBr_3 , et (iii) avec au moins un composé de boration.
2. Composition suivant la revendication 1, dans laquelle la réaction (i) est conduite avant les réactions (ii) et (iii).
3. Composition suivant la revendication 1, dans laquelle les réactions (ii) et (iii) sont conduites avant la réaction (i).
4. Composition suivant la revendication 1, dans laquelle les réactions (i), (ii) et (iii) sont conduites conjointement.
5. Composition suivant l'une quelconque des revendications 1 à 4, dans laquelle la réaction (ii) est conduite au moyen de l'acide phosphoreux ; et la réaction (iii) est conduite en utilisant (a) au moins un acide dérivé du bore ou un de ses anhydrides ou esters, ou (b) n'importe laquelle de leurs associations.
6. Composition suivant l'une quelconque des revendications précédentes, dans laquelle l'agent d'acylation utilisé dans la réaction (i) est l'anhydride maléique, l'acide maléique, l'acide fumarique, l'acide malique ou n'importe laquelle de leurs associations.
7. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le dispersant sans cendre azoté basique est un dispersant du type succinimide ayant un nombre moyen d'au moins 3 atomes d'azote par molécule.
8. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le dispersant sans cendre azoté basique est un dispersant du type succinimide formé à partir d'un agent d'acylation alkyl- ou alcénylsuccinique ayant un nombre moyen d'au moins 40 atomes de carbone dans le groupe alkyle ou alcényle et d'un mélange d'alkylène-polyamines ayant un nombre moyen d'au moins 3 atomes d'azote par molécule.
9. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le dispersant sans cendre azoté basique est un dispersant du type succinimide formé à partir d'un agent d'acylation polyisobuténysuccinique dérivé d'un polyisobutène ayant une moyenne numérique du poids moléculaire comprise dans l'intervalle de 500 à 10 000 et d'un mélange d'éthylène-polyamines comprenant des structures cycliques et des structures acycliques, ledit mélange ayant une composition globale moyenne proche de celle d'un mélange dans l'intervalle de la triéthylène-tétramine à la pentaéthylène-hexamine.
10. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le ou les agents diacides d'acylation sont utilisés en des quantités allant de 0,01 à 0,5 mole par équivalent moyen d'azote dans le ou les dispersants sans cendre azotés basiques, sous réserve que le produit résultant contienne au moins 0,05 équivalent d'azote basique et dans laquelle une quantité allant jusqu'à environ 5 % de phosphore, exprimée en pourcentage en poids de phosphore élémentaire et une quantité allant jusqu'à environ 5 % de bore, exprimée en pourcentage en poids de bore élémentaire, sont introduites dans le dispersant global final obtenu par coréaction.
11. Composition suivant l'une quelconque des revendications 8 à 10, dans laquelle le ou les agents diacides d'acylation sont utilisés en des quantités telles que le rapport molaire total (a) de l'agent diacide d'acylation plus (b) l'agent alcényl-succinique d'acylation utilisé dans la formation du succinimide initial soit compris dans l'intervalle de 1,5 à 3,5 moles de constituants (a) et (b) par mole de polyamine ; et dans laquelle 0,05 à 2,5 % de phosphore, exprimés

en pourcentage en poids de phosphore élémentaire, et 0,05 % à 2,5 % de bore, exprimés en pourcentage en poids de bore élémentaire, sont introduits dans le dispersant global final obtenu par coréaction.

- 5 12. Composition d'huile lubrifiante ou de fluide fonctionnel comprenant une proportion dominante d'une huile de viscosité propre à la lubrification et une petite quantité dispersante d'une composition de dispersant répondant à la définition suivant l'une quelconque des revendications 1 à 11.
13. Concentré d'additif contenant une composition de dispersant répondant à la définition suivant l'une quelconque des revendications 1 à 11.
- 10 14. Procédé de préparation d'une composition de dispersant, soluble dans l'huile, répondant à la définition suivant la revendication 1, qui comprend
 - 15 (a) la réaction d'un dispersant sans cendre azoté basique avec au moins un agent diacide d'acylation ayant jusqu'à 12 atomes de carbone dans la molécule, avec au moins un composé de phosphorylation choisi entre l'acide phosphoreux, l'acide hypophosphorique, l'acide métaphosphorique, l'acide pyrophosphorique, l'acide hypophosphoreux, l'acide pyrophosphoreux, l'acide phosphineux, l'acide tripolyphosphorique, l'acide tétrapolyphosphorique, l'acide trimétaphosphorique, POCl_3 , PCl_3 et PBr_3 , et avec au moins un composé de boration, ces réactions étant conduites conjointement ou successivement dans n'importe quel ordre ;
 - 20 (b) la réaction d'un dispersant azoté basique phosphorylé avec au moins un composé de phosphorylation choisi entre l'acide phosphoreux, l'acide hypophosphoreux, l'acide métaphosphorique, l'acide pyrophosphorique, l'acide hypophosphoreux, l'acide pyrophosphoreux, l'acide phosphineux, l'acide tripolyphosphorique, l'acide tétrapolyphosphorique, l'acide trimétaphosphorique, POCl_3 , PCl_3 et PBr_3 avec un agent diacide d'acylation ayant jusqu'à 12 atomes de carbone dans la molécule et avec au moins un composé de boration ;
 - 25 (c) la réaction d'un dispersant sans cendre azoté basique acylé avec un agent diacide d'acylation ayant jusqu'à 12 atomes de carbone dans la molécule avec au moins un composé de phosphorylation choisi entre l'acide phosphoreux, l'acide hypophosphorique, l'acide métaphosphorique, l'acide pyrophosphorique, l'acide hypophosphoreux, l'acide pyrophosphoreux, l'acide phosphineux, l'acide tripolyphosphorique, l'acide tétrapolyphosphorique, l'acide trimétaphosphorique, POCl_3 , PCl_3 et PBr_3 et avec au moins un composé de boration ; ou
 - 30 (d) la réaction d'un dispersant azoté basique boroné avec un agent diacide d'acylation ayant jusqu'à 12 atomes de carbone dans la molécule et avec au moins un composé de phosphorylation choisi entre l'acide phosphoreux, l'acide hypophosphorique, l'acide métaphosphorique, l'acide pyrophosphorique, l'acide hypophosphoreux, l'acide pyrophosphoreux, l'acide phosphineux, l'acide tripolyphosphorique, l'acide tétrapolyphosphorique, l'acide trimétaphosphorique, POCl_3 , PCl_3 et PBr_3 .
 - 35
- 15 15. Procédé suivant la revendication 14, dans lequel le dispersant azoté basique soumis au procédé est un dispersant du type succinimide formé à partir d'un agent d'acylation alkyl- ou alcényl-succinique ayant un nombre moyen d'au moins 40 atomes de carbone dans le groupe alkyle ou alcényle et d'un mélange d'alkylène-polyamines ayant un nombre moyen d'au moins 3 atomes d'azote par molécule.
- 40 16. Procédé suivant la revendication 14, dans lequel le dispersant azoté basique initial est un dispersant du type succinimide formé à partir d'un agent d'acylation polyisobutynyl-succinique dérivé d'un polyisobutène ayant une moyenne numérique du poids moléculaire comprise dans l'intervalle de 500 à 10 000 et d'un mélange d'éthylène-polyamines comprenant des structures cycliques et des structures acycliques, ledit mélange ayant une composition globale moyenne proche de celle d'un mélange dans l'intervalle de la triéthylène-tétramine à la pentaéthylène-hexamine.
- 45 17. Procédé pour lubrifier des pièces mécaniques, dans lequel une surface d'élastomère fluoré est en contact avec un lubrifiant ou fluide fonctionnel, procédé qui est mis en oeuvre au moyen d'une huile lubrifiante ou d'un fluide fonctionnel comprenant une composition de dispersant répondant à la définition suivant l'une quelconque des revendications 1 à 11.
- 50
- 55